FORMULATION AND METHOD FOR ACHIEVING METALLIC EFFECTS IN CERAMIC TILES AND THE APPLICATIONS THEREOF

Publication number: ES2161193

Publication date: 2001-11-16

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Classification:

- international: ***C03C8/08; C04B41/50; C04B41/86;*** **C03C8/00; C04B41/45; C04B41/86;** (IPC1-7): C03C8/02; C04B41/86

- european: C03C8/08; C04B41/50M; C04B41/86

Application number: ES20000000799 20000330

Priority number(s): ES20000000799 20000330

Also published as:

EP1306355 (A1)

WO0172651 (A1)

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Abstract not available for ES2161193

Abstract of corresponding document: **EP1306355**

The formulation comprises a mixture of essential oxides, namely: SiO2, Al2O3, Fe2O3 and P2O3, together with certain optional oxides, namely: CaO, MgO, Na2O and K2O; and it is free of noble metals. This formulation is applied to a carrier or ceramic tile by a conventional technique and it is subjected to a firing process by the single firing technique. The formulation has important uses and advantages in the sector of the ceramics industry.

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 306 355 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
02.05.2003 Bulletin 2003/18

(21) Application number: **00988820.7**

(22) Date of filing: **29.12.2000**

(51) Int Cl.[7]: **C03C 8/02**, C04B 41/86

(86) International application number:
PCT/ES00/00498

(87) International publication number:
WO 01/072651 (04.10.2001 Gazette 2001/40)

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **30.03.2000 ES 200000799**

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(54) FORMULATION AND METHOD FOR ACHIEVING METALLIC EFFECTS IN CERAMIC TILES AND THE APPLICATIONS THEREOF

(57) The formulation comprises a mixture of essential oxides, namely: SiO_2, Al_2O_3, Fe_2O_3 and P_2O_3, together with certain optional oxides, namely: CaO, MgO, Na_2O and K_2O; and it is free of noble metals.

This formulation is applied to a carrier or ceramic tile by a conventional technique and it is subjected to a firing process by the single firing technique.

The formulation has important uses and advantages in the sector of the ceramics industry.

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Description

TECHNICAL FIELD OF THE INVENTION

[0001] The present invention fits in the sector of the ceramics industry and in particular the sector of ceramic tiles provided with metallic effects.

[0002] More specifically, the present invention provides a new formulation for the obtainment of metallic effects on ceramic tiles as well as a process for the use of said formulation for the purpose of achieving the desired effects.

PRIOR ART OF THE INVENTION

[0003] Within the ceramics sector one of the aspects valued the most by consumers is the presence of metallic effects on ceramic tiles, which gives them an important added value as decorative elements.

[0004] Nowadays, the production of this type of effect is normally carried out by means of preparations that are combinations of noble metals with a varied structure and combination. Normally, the majority of these preparations are a combination of noble metals with sulfur and organic substances, for example, oleo-sulfide-resinous solutions. Among these products, lustrous preparations of gold, silver and/or platinum in the form of lacquers or pastes or else powdered products are mainly used. All of them are capable of burnishing the surface of the ceramic tile providing it with a metallic effect.

[0005] These preparations comprised of noble metals and sulfur, aside from having a very high cost, have problems of toxicity, some of them in themselves such as silver derivatives and others because they are frequently contaminated by mercury.

[0006] The process for using this type of preparation implies the application thereof on the already finished tile and the additional firing of the assembly at a low temperature, which is known as the third fire technique. It requires another special kiln in which this final firing is carried out. The use of ceramic kilns with a reducing atmosphere (traditional method) is also possible but the desired effects are not so good, as there is great instability in the obtained results, at the same time that polluting gases coming from the reduction process are given off.

[0007] In accordance with the above, it is obvious for an ordinary expert in the sector, that the decorative techniques used nowadays for the obtainment of metallic effects on ceramic tiles have serious inconveniences that can be summarized in the following points:

- High cost thereof due, on the one hand, to the raw materials used (metal nobles such as gold, silver or platinum); and on the other hand, due to the fact that these metals cannot be subjected to a high temperature firing cycle, needed for the obtainment of ceramic tiles by single firing, to the need for the obtainment of the desired final effect, of additional firing either in reducing atmospheres or at lower temperatures, which involves an additional manufacturing cost.
- Great environmental impact in the handling of the products as well as in the wastes produced in the process for the obtainment thereof.
- Low technical characteristics of this type of product, which do not provide good results with respect to compliance of the European rule EN-122 of chemical resistance of enameled ceramic tiles.
- Lack of stability with respect to the appearance and coloration of the ceramic tiles with metallized effects obtained with this type of product.

[0008] Therefore, it would be very desirable to be able to obtain some starting products and some techniques for applying them to ceramic tiles, that overcome the above-mentioned inconveniences.

[0009] The applicant has concentrated his research efforts along these lines and has achieved a new formulation applicable to ceramic tiles by single firing, which aside from overcoming said inconveniences provides additional important advantages in the sector.

[0010] Therefore, an object of the present invention is to provide a new formulation used to provide metallic effects on ceramic tiles manufactured by single firing.

[0011] Another object of the present invention is to provide a process for the use of said formulation for the obtainment of ceramic tiles by single firing with metallic effects.

[0012] Another object of the present invention is ceramic tiles with metallic effects obtained from said formulations using the process of single firing of the present invention.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0013] The present invention refers to a new formulation for the obtainment of metallic effects on ceramic tiles, to the process of use of said formulation in order to obtain said effects and to the tiles obtained thereby.

[0014] More specifically, the present invention refers to a formulation for the obtainment of metallic effects, similar or superior to the ones achieved with the preparations comprised of noble metals with respect to luster, coloration and intensity, durability and stability of the metallic effect on the ceramic tile.

[0015] The formulation is applicable in general to ceramic tiles for ceramic pavings and coverings.

[0016] The formulation, free of noble metals, is comprised of silicon, aluminum, iron and phosphorus oxides and can optionally contain calcium, magnesium, sodium and potassium oxides.

[0017] This formulation is a preparation for the decoration of ceramic tiles that, once same has been applied to the carrier or ceramic tile, and fired in an industrial

kiln, with the conventional single firing cycle of this type of ceramic tile, gives rise to effects similar or superior to those that formulations comprised of noble metals produce, with respect to the metallic appearance as well as to coloration, luster and metallic sheen.

[0018] The oxides comprising the formulation of the invention, as it is well known, are classified as nontoxic and safe products.

[0019] Among the above-cited oxides, silicon, aluminum, iron and phosphorus oxides are "basic or substantial". In turn, calcium, magnesium, sodium or potassium oxides are optional and they can be considered as "excipients or unsubstantial", although it should be made clear that their presence can provide certain desirable properties to the final formulation, such as fusion capacity, although they are not essential for the obtainment of the desired metallic effect.

[0020] The proportions (percentages by weight with respect to the weight of the final product) of each one of said oxides, that comprise the formulation of the invention are indicated in the following Table 1.

TABLE 1

SiO_2	30-55%
Al_2O_3	7-21%
Fe_2O_3	10-30%
P_2O_5	7-27%
CaO	0-7%
MgO	0-6%
Na_2O	0-8%
K_2O	0-8%

[0021] The formulation of the invention comprised of this mixture of oxides, can have different forms well known in the ceramics sector, for example: frit, granule or pellets, enamel, micronized material, solution for serigraphy, etc. In any of the forms, the process for the obtainment of the metallic effect implies the application of the formulation to the tile to be decorated and the firing of the assembly in a conventional industrial kiln for single firing.

[0022] More specifically, in the event that the formulation of the invention has the form of a frit, the mixing of said oxides is carried out first of all by means of fusing them at a high temperature. Then the frit is mixed with water and homogenized in order to obtain a suspension. The suspension thus obtained is applied to the carrier or ceramic tile by means of any conventional application technique and finally it is fired in an industrial kiln following the regular firing cycle of the ceramics sector (namely, 1,100-1,250°C for 40-90 minutes) of the ceramic tile by single firing, for paving as well as for covering.

[0023] In the event that the formulation of the invention has the form of granules or pellets, they are obtained by dry treatment of the cited frit. The granules or pellets thus obtained are applied directly to the ceramic tile in the form of granules. Then the assembly is subjected to the thermal firing cycle of the ceramic tile, in the cited single firing conditions.

[0024] In the event that the formulation of the invention has the form of enamel, the mixing of the starting oxides is carried out at room temperature in an aqueous medium, with subsequent homogenization and application of the suspension to the carrier or tile, by means of any enameling technique of ceramic tiles such as bell, disk or aerograph techniques. Then the thermal firing cycle is applied to the tile provided with enamel.

[0025] In the event that the formulation of the invention is serigraphy, the enamel obtained by mixing in an aqueous medium at room temperature and subsequent homogenization, is dried and micronized. Then, the micronized product thus obtained is mixed with a polyglycol type serigraphic vehicle and is applied to the ceramic tile with the help of appropriate serigraphic screens. Finally the serigraphed ceramic tile is subjected to the thermal firing cycle.

[0026] The formulations of the invention provide many innovations and advantages in comparison to decorations carried out by adding noble metals and the use of reduction or specific firing techniques at a lower temperature. Among these advantages the following should be pointed out:

- Lower cost of the raw materials used in the manufacturing thereof and therefore greater competitiveness of the obtained products.
- High technical characteristics of the obtained ceramic products in compliance of the regulations in force and of the market requirements.
- Lower environmental impact of the formulations and decoration system of the invention with regard to toxicity thereof and the wastes that can be produced.
- Adaptability to the line of products presented to the majority of current technologies for manufacturing tiles, without the need to include special machines in order to achieve the desired effects.
- Great stability and versatility of the products.
- Wide range of products adaptable to the different decoration techniques used nowadays by the ceramics industry for the production of pavings and coverings, such as enameling (in their different types: bell, disk or gun), serigraphy, dry applications, etc.

EMBODIMENTS OF THE INVENTION

[0027] The present invention is additionally illustrated by means of the following examples, which should not be considered as a limitation or restriction of the scope thereof.

EXAMPLE 1

[0028] The following oxides in the indicated proportions (percentage by weight with respect to the total mixture of oxides) were mixed with 90 g of water:

SiO_2	39.41%
Al_2O_3	12.56%
Fe_2O_3	14.74%
P_2O_5	20.93%
CaO	5.16%
Na_2O	6.42%
K_2O	0.72%

[0029] The obtained aqueous suspension was homogenized by grinding. 6 g of the resulting suspension were applied, by means of the gun application technique or aerograph technique to a 15x15 cm porcelain stoneware ceramic tile. An amount of 1.3 g of solid per each 100 cm^2 remained on the tile.

[0030] The tile was allowed to dry and once it was dry it was subjected to a firing cycle in an industrial kiln at 1,200°C for 80 minutes.

EXAMPLE 2

[0031] The following oxides in the indicated proportions (percentage by weight with respect to the total mixture of oxides) were mixed with 90 g of water:

SiO_2	37.40%
Al_2O_3	12.23%
Fe_2O_3	18.78%
P_2O_5	19.24%
CaO	5.15%
Na_2O	6.42%
K_2O	0.72%

[0032] The obtained aqueous suspension was homogenized by grinding. Then the mixture was dried at 115°C. Once it was dried, it was micronized. 50 g of the micronized mixture were weighed and 40 g of serigraphic vehicle (polyglycol) were added. After the mixture was homogenized, it was applied to a flat 48 thread serigraphy screen.

[0033] The serigraphed tile was allowed to dry and subjected to a firing cycle in an industrial kiln at 1,180°C for 65 minutes.

EXAMPLE 3

[0034] The following oxides were mixed together in the percentages by weight that are indicated with respect to the total weight thereof:

SiO_2	38.28%
Al_2O_3	12.59%
Fe_2O_3	14.74%
P_2O_5	20.94%
CaO	5.06%
Na_2O	0.59%
K_2O	7.73%

[0035] This mixture was introduced into a fusion kiln and kept at 1,450°C for 45 minutes. Then the resulting fused material (frit) was cooled at room temperature and dried by a conventional method, for example, in a laboratory oven at 100-110°C, or by means of a drying lamp. The dry mixture was granulated (pelleted) with the help of a battery of sieves, taking different fractions of the granulated sample of a size between 0.1 and 1 mm. Then the granule thus obtained was applied to a ceramic tile using granule glue as an adhering agent.

[0036] The tile was allowed to dry and subjected to a firing cycle in an industrial kiln at 1,200°C for 80 minutes.

[0037] The ceramic tiles obtained in these three examples had, by a visual comparison, a similar luster, sheen and coloration as that of tiles treated with metals obtained by the third fire technique or any other method of the prior art.

Claims

1. Formulation for the obtainment of metallic effects on ceramic tiles manufactured by single firing free of noble metals **characterized in that** it essentially comprises a mixture of SiO_2, Al_2O_3, Fe_2O_3 and P_2O_5.

2. Formulation according to claim 1, **characterized in that** aside from the cited oxides the formulation can optionally include CaO, MgO, Na_2O and K_2O.

3. Formulation according to any of claims 1 and 2, **characterized in that** said oxides form part of said formulation in the following percentages by weight, with respect to the total weight of the mixture:

SiO_2	30-55%
Al_2O_3	7-21%
Fe_2O_3	10-30%
P_2O_5	7-27%
CaO	0-7%
MgO	0-6%
Na_2O	0-8%
K_2O	0-8%

4. Formulation according to claim 3, **characterized in that** the essential oxides are in the following per-

centages:

SiO_2	35-52%
Al_2O_3	11-18%
Fe_2O_3	10-22%
P_2O_5	12-25%

5. Formulation according to any of the preceding claims **characterized in that** it has the form of a frit, granule, enamel or micronized material.

6. Process for manufacturing decorated ceramic tiles provided with metallic effects, **characterized in that** it comprises applying one of any of the formulations of preceding claims 1 to 5 on the ceramic tile to be decorated and firing the tile in an industrial firing kiln in a firing cycle between 1,100-1,250°C for 40-90 minutes.

7. Ceramic tiles with metallic effect **characterized in that** they are obtained by the process of claim 5.

8. Use of the formulation of claims 1 to 5 for the manufacture of decorated ceramic tiles with metallic effects by single firing.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/ ES 01/00498

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 :C03C 8/02, C04B 41/86
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 : C03C, C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPODOC, WPI, CIBEPAT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	ES 2125112 T (CERDEC AKTIENGESELLSCHAFT KERAMISCHE FARBEN) 16.02.1999 (16 February 1999), column 1, line 3-24, column 3, lines 44-60, column 4, lines 29-33.	1, 2, 5
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A	EP 205048 A (MERCK PATENT) 17.12.1986, the whole document	1-8

☐ Further documents are listed in the continuation of box C. ☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
23 March 2001 (23.03.2001)	18 April 2001 (18.04.2001)
Name and mailing address of the ISA/ SPTO	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No
PCT/ ES 00/00498

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